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Control Growth Of Zno Nanorods By Chemical Bath Deposition: Study On Heat Treatment Effect

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ABSTRACT: Chemical Bath Deposition (CBD) is a simple aqueous solution and easy and reproducible method employed for systematically growth of zinc oxide (ZnO) thin film on glass substrate. The investigations on the effect of annealing temperature on the structural, optical properties and morphology of ZnO nanorod deposited by chemical bath deposition have been carried out. The films were specula and adherent to glass substrate. It is found that, annealing temperature significantly influence the quality of ZnO thin films. We proceeded to anneal ZnO films in air for 60 min from 150ºC to 300 ºC. X-ray diffraction (XRD) pattern showed that the deposited ZnO thin films was exhibited a polycrystalline structure of the wurtzite with monophasic of hexagonal shaed naorods. No other phases were observed in XRD pattern. ZnO lattice crystals transformed from agglomerated random growth to long-and-slim hexagonal rods as observed by scanning electron microscopy (SEM).This approach can provide a novel and simple route to obtain ZnO nanostructures hexagonal rods, which may improve the properties of nanostructure based devices.

Keywords: Chemical bath, Structural, optical properties, wurtzite, ZnO nanorod

1. Introduction

Zinc oxide (ZnO) nanorods have been widely studied due to their remarkable performance in nanodevoces based on them. ZnO nanorods morphology has received a great deal of attention in recent years, because of its unique optoelectronic, mechanical, magnetic and chemical properties provide various potential applications [1]. ZnO possesses variety of nanostructures and it is the next most important material followed by carbon nanotubes [2]. Various chemical and physical deposition techniques have reportedly created an oriented structure of ZnO nanorods with average diameters typically ranging over an order of magnitude from 20 to 200 nm. For instance, catalytic growth via the liquid-solid-vapor epitaxy (VLSE) mechanism [3], metal-organic chemical vapor deposition (MOCVD) [4], pulsed laser deposition (PLD) [5] and chemical spray [6] have been particularly successful in creating highly oriented arrays of nanorods of ZnO. Out of these, Chemical Bath Deposition is a soft chemical method to deposit ZnO nanforms. However, development of nanosized ZnO seed coating of a substrate [7] or template [8] are the prerequisite conditions for the growth of vertically aligned ZnO nanorods.

In the present work, we are particularly successful in creating vertically aligned ZnO nanorod arrays. The strategy to design nanostructured thin film is entirely based on a wet chemical, bottom up approach to create nanoparticles or to control their orientation. The optimized preparative parameters were used to grow vertically aligned ZnO nanorods. The deposited ZnO films were characterized for their structural, surface morphological, electrical and optical properties.

2. Experimental details

An aqueous solution of 0.1 M $Zn(NO_3)_2$ was prepared, and to this solution aqueous NH_3 solution was added under constant stirring to maintain the pH-12 of the solution. A white precipitate was initially observed, which subsequently dissolved upon further addition of NH_3 solution. The solution was prepared with disinfect water to observe the stability of dissolved ions. A pre-cleaned glass substrate was immersed and placed vertically in the solution. The preparative parameters employed for the present study are shown in the table.

Chemical Parameters	Solvent	Bath Temperature	pH	Concentration of $Zn(NO_3)_2$	Reactive reaction time	Annealing Temperature
Preparative Parameters	Disinfected distilled water	80 ^{0}C	12	0.1M	2 Hrs	200^{0}C-300^{0}C

The substrates, with the deposited ZnO nanorods, were thoroughly washed with deionized water to eliminate residual salts [9]. These films were annealed from 200ºC–300ºC for 2 h at the steps of 50^0C and used for the further characterization. A Philips Japan MPD 1880 X-ray powder diffractometer was employed to study the crystal structure of the films. Surface morphology of the films was examined by scanning electron microscopy, SEM (JEOL, 15 kV). A Shimadzu double beam spectrophotometer was employed for obtaining transmittance in the wavelength range of 350–900 nm and to evaluate the direct band gap energies.

3. Results and discussion

In chemical method, the small degree of supersaturation causes the heterogeneous nucleation of the metal oxide on the substrates [10]. The growth and formation of nuclei decide the reactive reaction time and concentration of the precursor solution. For Zn^{2+} aqueous solution, the necessary condition for the formation of precipitation is the establishment of ion product higher than solubility product of $Zn(OH)_2$. The supersaturation can be controlled by optimizing the preparative parameters such as bath temperature, pH and concentration of resultant solution, to get nanocrystalline thin films. For the depositionof ZnO, the mechanism of ZnO film formation can be elucidated as follows: $Zn(NO_3)_2$ was used as a source of Zn^{2+} ions. When ammonia was added to it, white precipitate of $Zn(OH)_2$ was occurred, further addition of ammonia resulted in to dissolution of $Zn(OH)_2$ in to the solution and formation of zincate ($[Zn(NH_3)_4]^{2+}$). The thermal decomposition of $[Zn(NH_3)_4]^{2+}$ releases ions of Zn^{2+} ions reacts with OH^- in the solution and results in the formation of $Zn(OH)_2$ or ZnO particles. As a result, the growth along the (002) plane has faster growth rate than that along other directions. This polarity causes the (002) face of the crystal either positively or negatively charged. In either case, surface will attract ions of opposite charges (O^{2-} or Zn^{2+}) to it, and this new surface covered with ions will in turn attract ions with opposite charges to cover the surface next and thereby reacting to form ZnO nanorods [11].

Figure (1) shows the XRD patterns of as deposited and annealed films of chemical bath deposited ZnO films with different annealing temperatures. The XRD technique helps to ensure identification and purity of the deposited film. X-ray diffraction (XRD) pattern show all diffraction peaks can be indexed as ZnO crystal with hexagonal wurtzite structure (JCPDS card no. 36-1451). From the recorded spectra, the main diffraction peak of (002) shown in figure, revealed the c-axis preferred orientation of the ZnO films. It is also interesting to note that, the increase in annealing temperature diffraction intensity of the peak, assigned to (002) orientation, is markedly increased and that from the other orientations are found to be emerged in weaken peak intensity. The alignment is as good as those obtained in earlier studies of ZnO nanorods grown by low temperature solution method [12], wherein the substrates used were preceded with ZnO nanoparticles in order to provide nucleation sites.

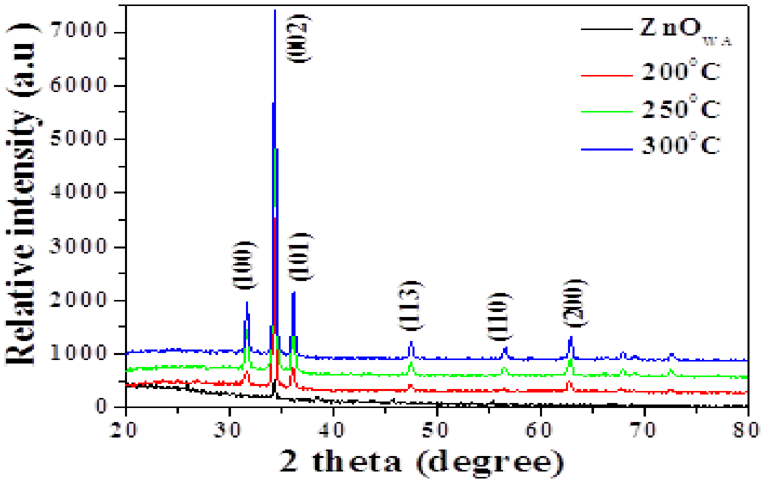

Fig.1: X-ray diffractograms of ZnO without and with annealed samples at 200ºC, 250 ºC and 300 ºC.

The further structural characterization, studied by the SEM micrographs, with two different magnifications of deposited ZnO films as shown in figure 2(a-f).

The morphology of the ZnO nanorods grown by CBD, is presented as high oriented hexagonal columnar nanorods structure with average primary topface size of 150nm (fig, 2f). It is clearly seen that the hexagonal shape grains occupy the entire surface of the film with its near stoichiometric composition. Agglomerated nanorod formation in without annealed sample tuned towards well defined hexagonal nanorod; typically having diameter ~300 nm observed for annealed sample at 300ºC. The annealing plays an important role that causes crystal to orient perpendicular to the substrate surface, as shown in Figure 2 (c-d).

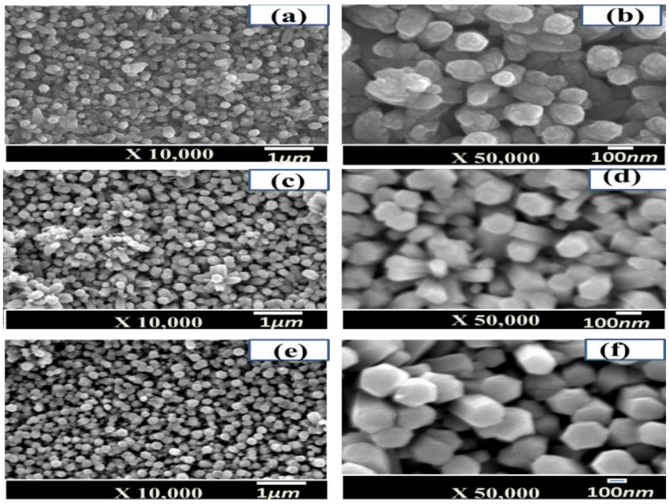

Fig. 2. Scanning electron micrographs of ZnO: (a-b) without annealed, (c-d) 250ºC annealed and (e-f) 300ºC annealed samples at two different magnifications (x 10,000 and x 50,000).

In order to confirm the presence of Zn and O in the synthesized ZnO nanorods, EDX measurements were performed. Figure (3) shows the representative EDX spectra of ZnO sample annealed at 300°C. From the similarity of the Zn and O peak intensity line traces, it is clear that after the synthesis process, zinc and oxygen were homogenously distributed inside the nanorod. From the EDX line traces it can be also concluded that O was successfully substituted in to the crystal structure of ZnO nanorods. The estimated amount of atomic weight percentages of Zn and O in deposited thin film are approximately 71.84% and 28.15%

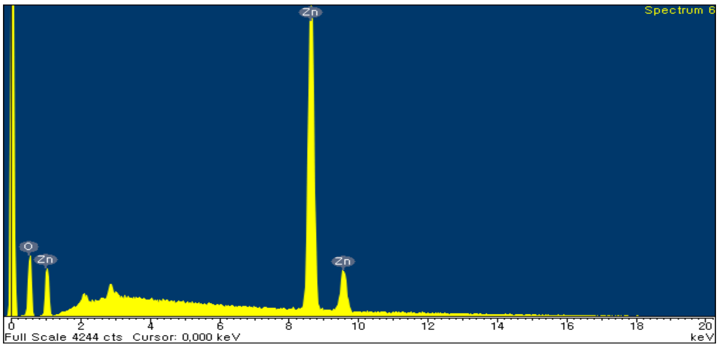

Fig. 3. EDAX of ZnO thin films of sample annealed at 300°C.

X-ray photoelectron spectroscopy has been considered to be a useful way to characterize valence state of ions, especially the surface state of materials. In order to detect the valence state of ZnO nanorods, high resolution XPS of Zn and O ions are measured. As shown in figure 4(a) the binding energy located at the 1021.6 ev and 1044.7 eV can be attributed to the 2p3/2 and 2p1/2 of Zn ions, similar with the previous report [13], which confirms the bivalence state of Zn ions. Furthermore figure 4(b) show the high resolution XPS of O 1s. According to the previous reports, the O1s state always contains three binding energy components [14]. So the typical O1s peak of our sample can be fitted into three Guassian peaks, which centre at 530.18 eV, 531.16ev, 532.57eV, corresponding to the low binding energy peak, middle binding peak and high binding energy, respectively XPS represents that at 300^{0}c the ZnO is completely formed

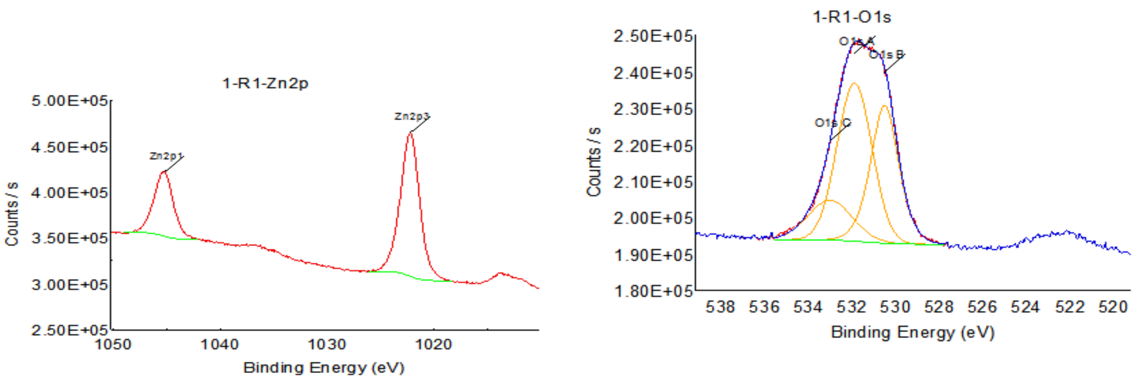

Fig. 4. XPS spectra of ZnO thin film annealed at 300^{0}c

The UV-vis absorption spectra of without and with annealed ZnO samples, were studied at room temperature.

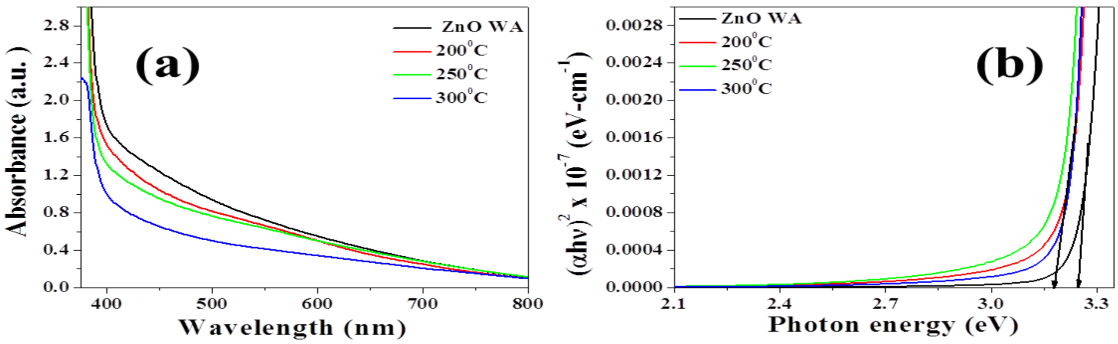

Fig. 6. (a) The variation of absorbance (αt) with wavelength (λ) and (b) Plots of $(\alpha h\upsilon)^2$ verses photon energy of ZnO without annealed and annealed at at 200ºC, 250 ºC and 300 ºC.

The absorption spectra figures 5(a) reveal that, all the samples have low absorbance in the visible region of the solar spectrum. The absorber edge of the ZnO films was found to shift towards shorter wavelength side with corresponding increase in annealing temperature. However, with increased annealing temperature, the absorbance is lowered with 'blue shift' in the absorption edge. The decreased absorbance with increased annealing temperature can be attributed to the decrease in the film thickness. The similar type of effect on the optical properties of ZnO thin films has been studied by R. Chandramohan et al. [15]. The optical band gaps of the ZnO films were calculated with $[(\alpha h\nu)^2 = A(h\nu - Eg)]$ from the absorption spectra correspond to electron excitation from the valence band to the conduction band and is shown in Figure 5(b). The band gap is found to be decreased from 3.24 to 3.18 eV with increased annealing temperature. The 'Eg' values are in good agreement with value reported for ZnO nanorods [16].

4. Conclusion

In summary, we have demonstrated an effective approach for controlled fabrication of ZnO nanorods morphology grown onto glass substrate by CBD method via annealing route. The possible growth mechanism for the vertically aligned ZnO nanorods is proposed. The annealing strongly affects structural, morphological and optical properties. Crystallites strongly oriented along (002) plane with increased annealing temperature showing textured growth along c-axis were composed of close-packed columnar rods. Morphological study revealed entangled hexagonal nanorods oriented vertically upwards hexagonal top front elevation with increased annealing temperature. The value of optical direct band gap was found to decrease from 3.24 to 3.18 eV**,** as the annealing temperature is increased. The controlled nanostructure ZnO hexagonal top front elevation nanorod morphology is ready to lend to design novel spintronic nanodevices.

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